Introduction to fuel cells: Fundamentals of electrochemical kinetics, thermodynamics and solid state chemistry for the experienced (I)

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Introduction to fuel cells: Fundamentals of electrochemical kinetics, thermodynamics and solid state chemistry for the experienced (I)

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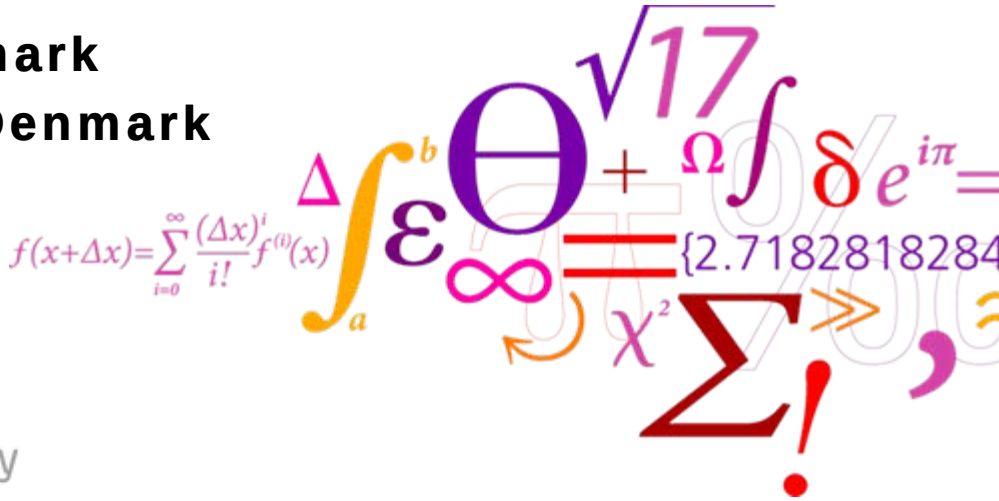

Risø DTU
National Laboratory for Sustainable Energy

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Brief introduction to SOFC materials

- All electrochemical cells consists of two electrodes separated by an electrolyte
- The electrodes must be good electron conductors
- The electrolyte must be a good ion conductor and ideally an electron insulator
- Incredibly many designs have been tested as presented previously
- The precise demands to the materials will to some extent depend on the design. I will present the demands as relevant for the bi-polar flat plate design

SOFC materials

- **Electrolyte**: often $Zr_{0.84}Y_{0.16}O_{1.92}$ (= 8YSZ), or another oxide ion conductor, or a proton conducting oxide
- **Fuel electrode**: often a porous Ni-YSZ cermet - often 40 % Ni + 60 % YSZ on a volume-of solids-basis with ca. 30 % porosity or all ceramic anode e.g. $La(Sr)Cr(Mn)O_3$
- **Oxygen electrode**: often a mixture of YSZ and LSM (= lanthanum strontium manganate), e.g. $(La_{0.75}Sr_{0.25})_{0.95}MnO_3$. Again often 40/60 volume ratio with ca. 30 % porosity; or mixed conducting perovskite, e.g. $(La_{0.6}Sr_{0.4})_{0.98}Fe_{0.8}Co_{0.2}O_3$ (LSFC)
- A wealth of other possibilities exist

Example of anode-supported cell dimensions

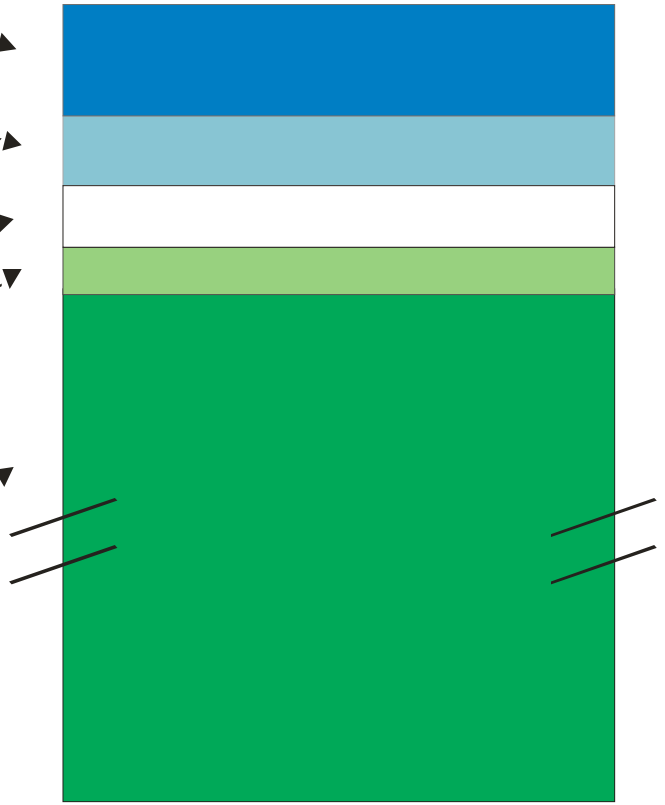
Cathode current collector, LSM, ~40µm

Electrochemically active cathode layer, LSM/YSZ, ~20µm

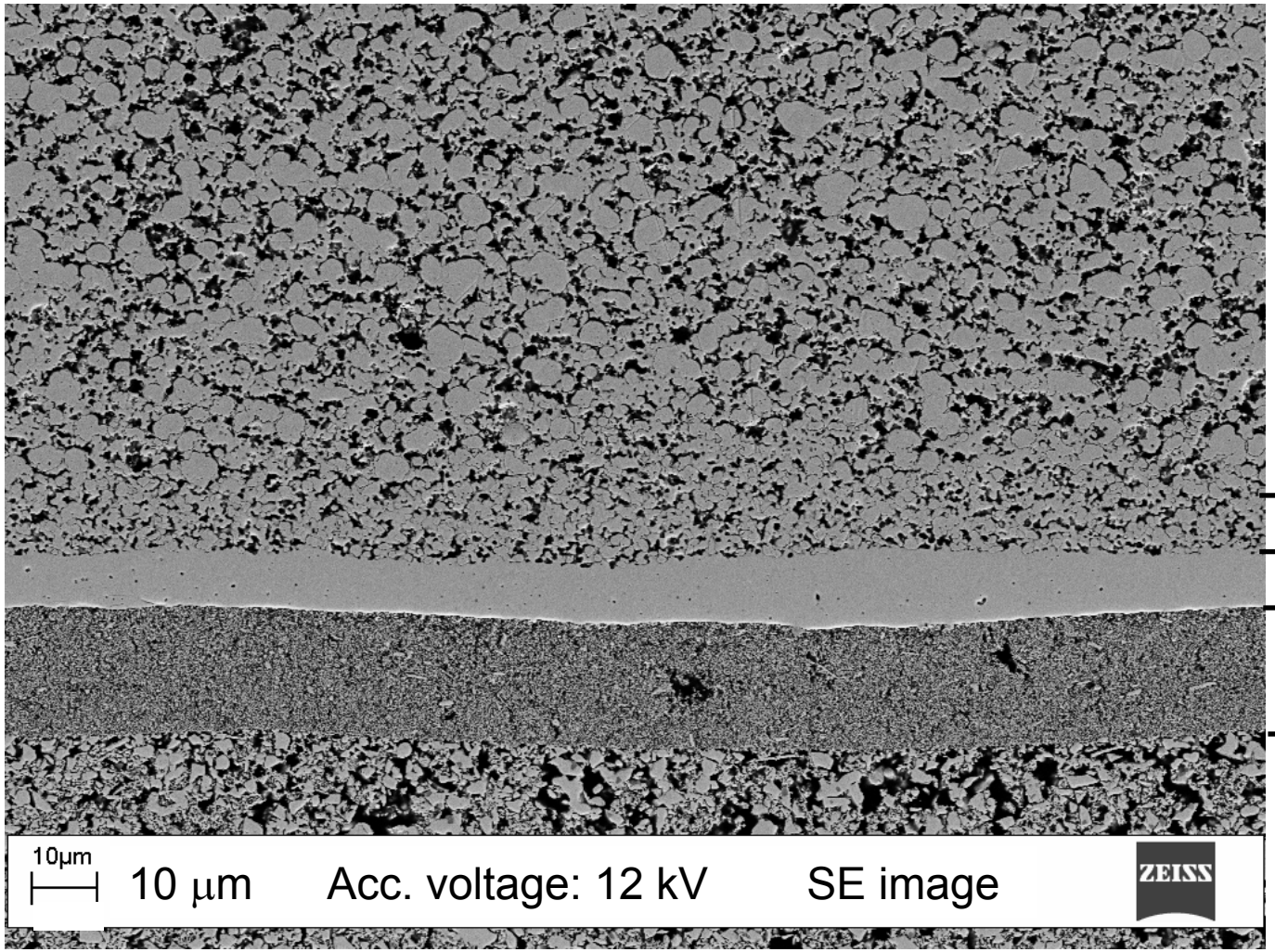
Electrolyte, YSZ, ~10µm

Electrochemically active anode layer, NiO/YSZ, ~15µm

Anode current collector (support), NiO/YSZ, ~300µm



Ni-YSZ supported cell



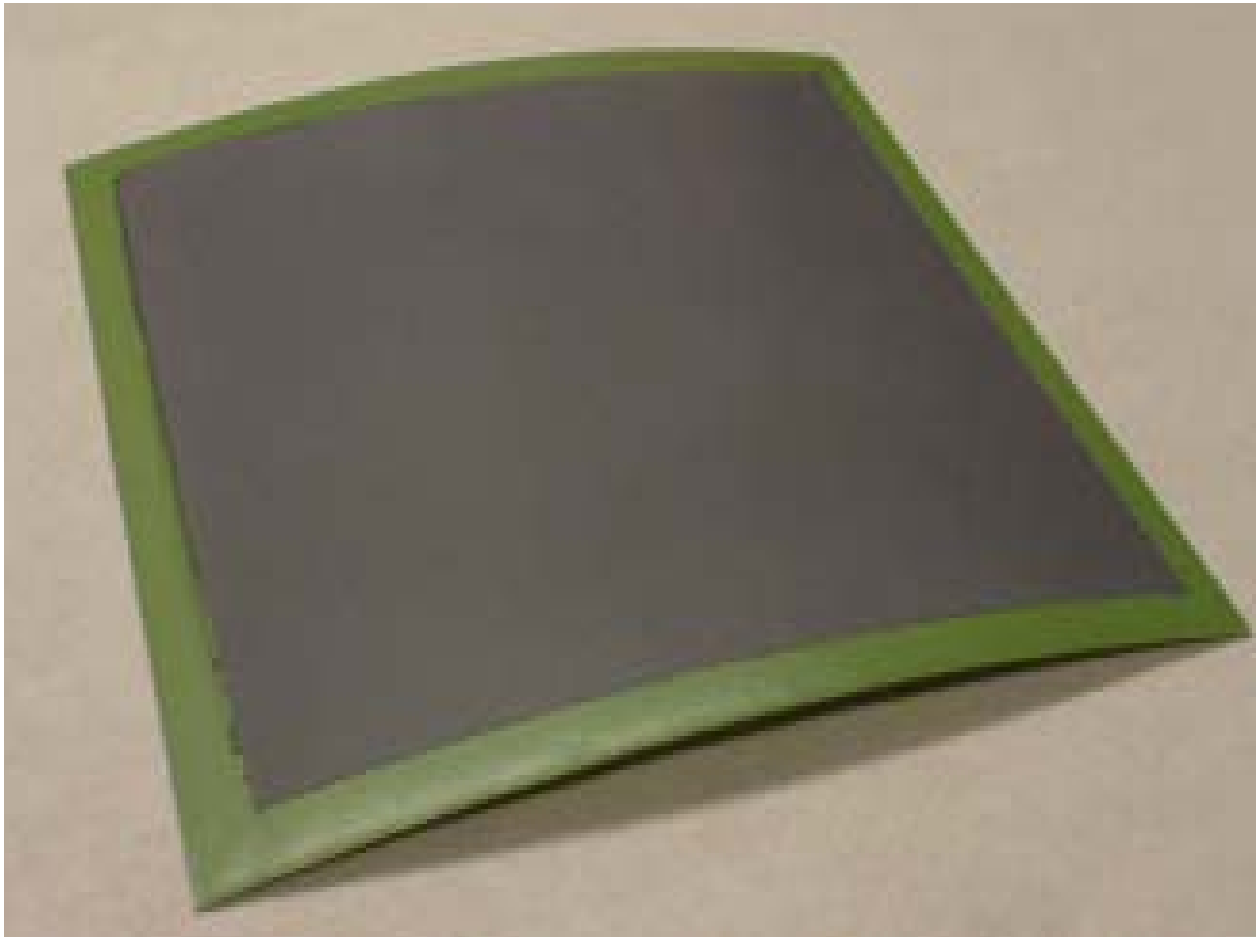
Ni/YSZ support

Ni/YSZ electrode

YSZ electrolyte

LSM-YSZ electrode

2G Risø SOFC



Active cell area 4x4 cm² for testing
Mainly 12 x 12 cm² cells for stacks
18 x 18 cm² are produced on a routine basis

List of requirements to an electrode in an SOFC

Requirement	Reason	Comment
Dimensional and thermodynamically stability at relevant temperatures and p_{O2}	Technology	Example: For the anode at 900 °C from 10^{-18} atm to 0.2 atm O_2
Good thermal expansion coefficient (TEC) matching with other cell and stack materials	Technology	In particular to that of the load bearing structural element of the cell (or cell stack)
Good adhesion and electrical (ionic) contact to the electrolyte	Technology	
Chemical compatibility with other cell and stack components	Technology	Both during cell fabrication (sintering), stack assembly and operation

List of requirements to an electrode in an SOFC (cont.)

Requirement	Reason	Comment
Polarization resistance $< 0.1\ \Omega cm^2$	Economy	Price is almost linear dependent on the polarization resistance
Electronic conductivity > 100 S/cm	Economy	To assure efficient current collection. The actual value is design dependent
Tolerance to natural available fuels (SOFC anode)	Economy	To avoid expensive fuel cleaning
Inexpensive materials and applicability of low-cost fabrication process	Economy	To make the device commercially viable

Requirements to an SOFC electrolyte

- **Economic reasons: Area specific resistance < 0.1 Ωcm^2 $\Rightarrow$ Low electrical resistance $\Rightarrow$ high specific ionic conductivity of the electrolyte material and/or a very thin electrolyte layer**
- **Very low electronic conductivity to avoid internal electronic leaks.**
- **Stable in both hydrogen and oxygen**
- **TEC matching with other cell and stack materials**

Types of SOFC materials

- Main group of materials are metal oxides with perovskite and fluorite structures – much more about them later.

- Other potential electrolyte type are:

- Apatite structured oxides, such as doped $La_{9.33}Si_6O_{26}$ and $La_{9.33}Ge_6O_{26}$ are good O^{2-} conductors, see e.g. Marrero-López et al., J. Power Sources, 195 (2010) 2496; or Slater et al., Annu. Rep. Prog. Chem., Sect. A, 99 (2003) 477; 102 (2006) 482 and 106 (2010) 429.

- $La_2Mo_2O_9$ & derivatives – LAMOX: good oxide-ion conductivity, but LAMOX has a tendency to get reduced in hydrogen – maybe a good anode material, see e.g. J. Jacquens, …, P. Lacorre, Fuel Cells, 10 (2010) 433

Fluorites and perovskites

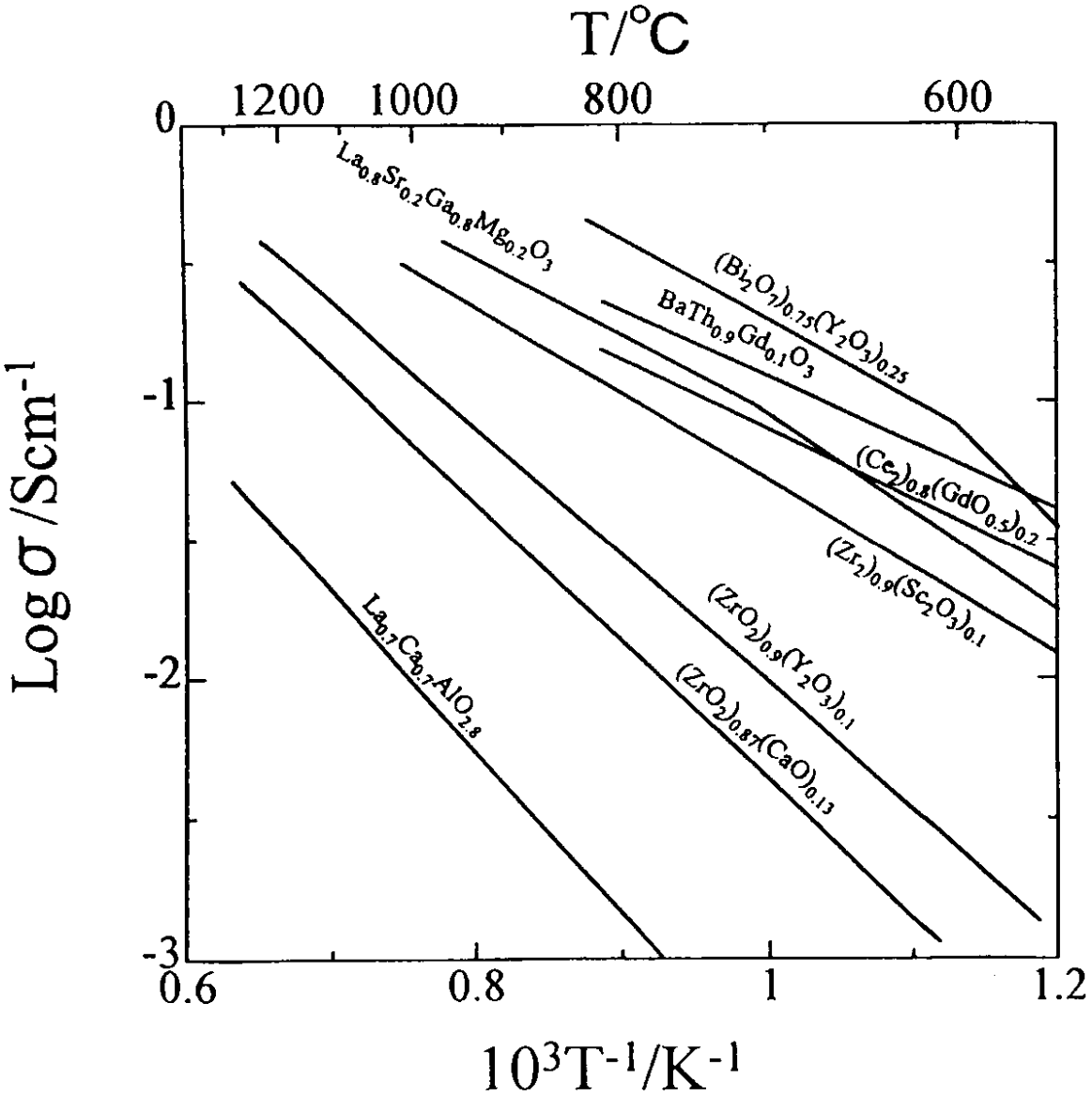
- Metal oxides with fluorite (MO_2, M = Zr, Ce, Hf, Th, U) and perovskite (ABO_3, A = large cation, B = small cation) related structures are very popular materials in R&D of SOC electrodes during these years, because:

- These compounds may have good electronic and ionic conductivities and are extremely flexible with respect to substitution of host cations and non-stoichiometry ⇨ possibility of materials engineering, i.e. tailoring the basic materials properties.

- In particular, large defect concentrations can be induced. This determines the properties to a large extent.

- Especially for the perovskites, an almost infinite number of possible combinations of multi-substitutions of metal ions on both A and B sites can be performed.

Example 1a – electrolyte conductivity

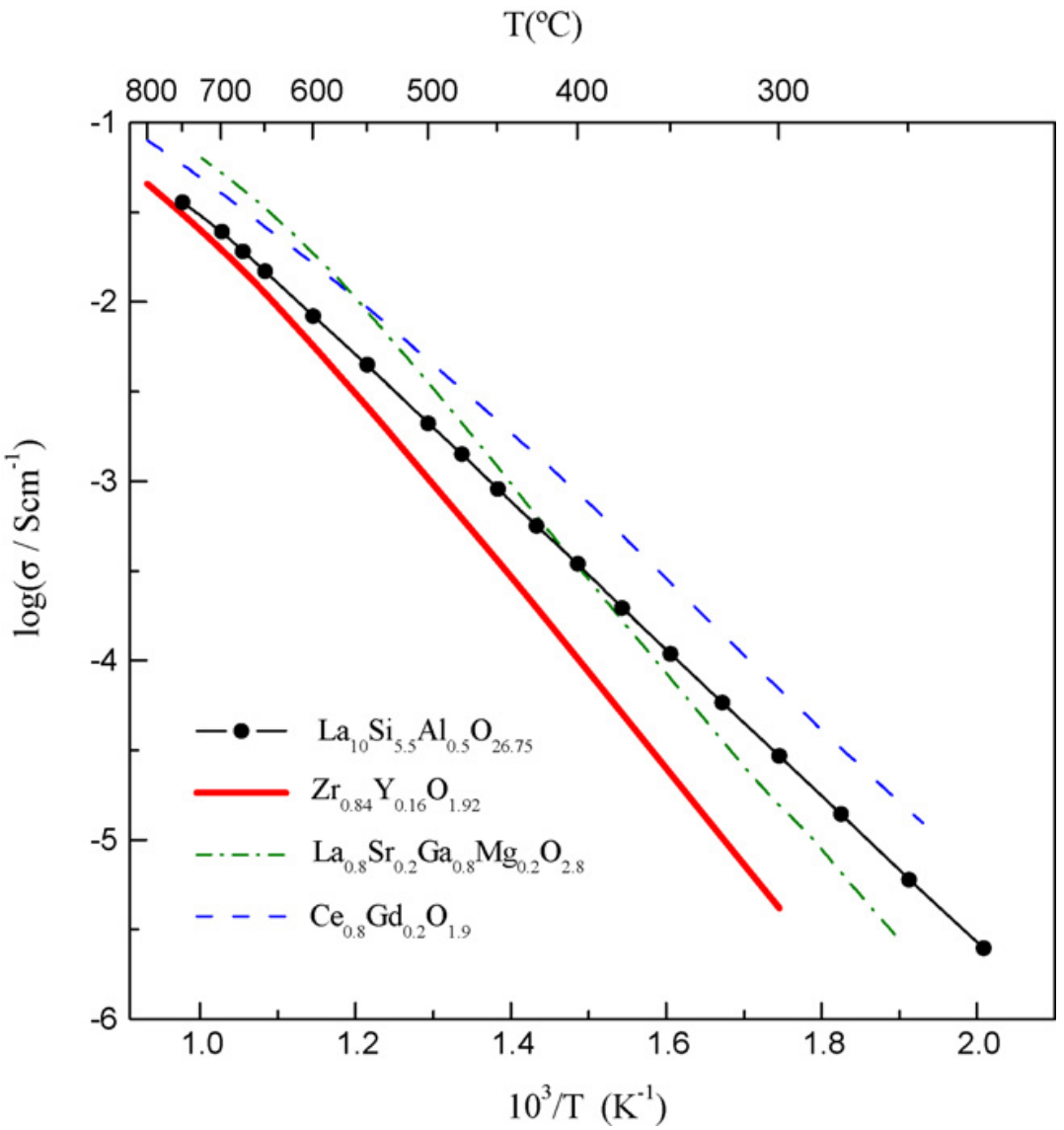


From: Ishihara, Sammes and Yamamoto, in: ***High Temperature SOFCs, Fundamentals, Design and Applications***, Eds. Singhal & Kendall, Elsevier 2003, p.84

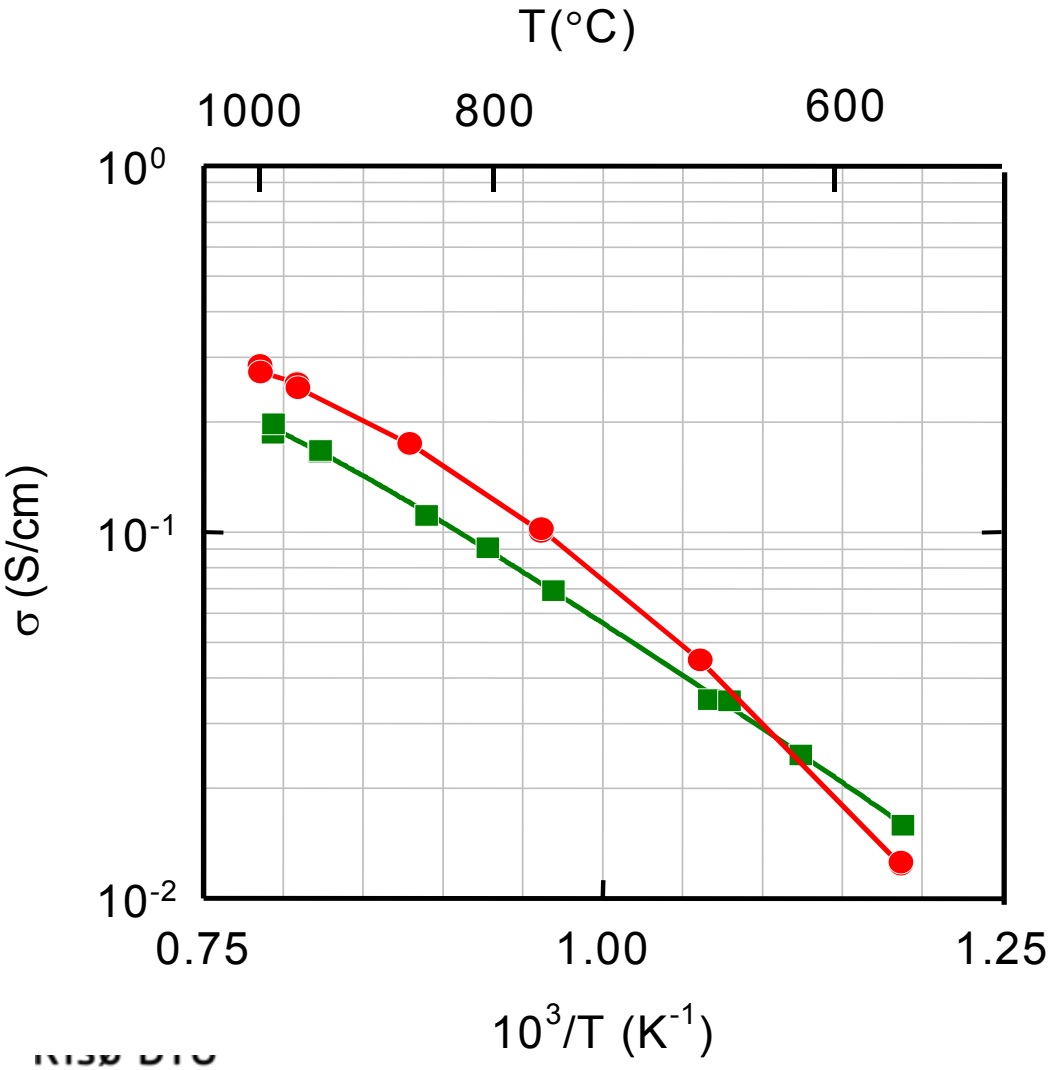
Example 1b – electrolyte conductivity

Arrhenius plot of the conductivity of $La_{10}Si_{5.5}Al_{0.5}O_{26.75}$ and different commercial solid electrolyte materials: $Zr_{0.84}Y_{0.16}O_{1.92}$ (Tosoh), $Ce_{0.8}Gd_{0.2}O_{1.9}$ (NexTech) and $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ (Praxair).

From: Marrero-López et al., J. Power Sources, 195 (2010) 2496



Example 1c – electrolyte conductivity



Arrhenius plot of the conductivity in air of:

$Ce_{0.9}Gd_{0.1}O_{1.95}$ (■)

and

$Zr_{0.79}Ce_{0.01}Sc_{0.20}O_{1.9}$ (●)

Any questions so far?

A question from me

If we wish a leak electronic current less than 1 mA cm^{-2} in a cell with a 10 μm electrolyte then what is the highest allowable average specific electronic conductivity (in S cm^{-1}) of the electrolyte material?

Solid state chemistry of fluorites and perovskites

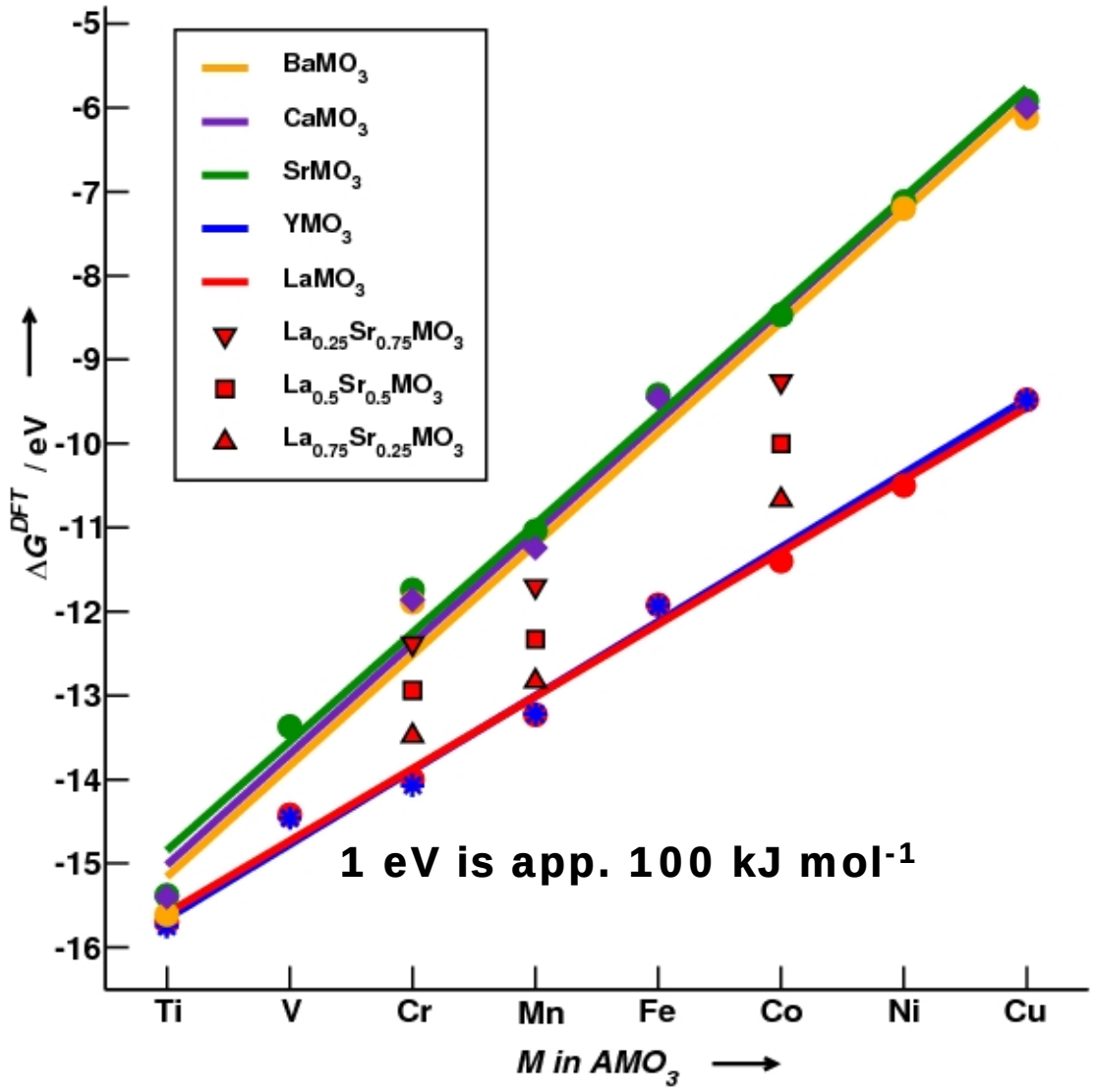
- The two relevant fluorites, stabilized zirconia and doped ceria are very stable materials with free energy of formation values of

- $\Delta G^0_{f,ZrO2}$ =

- $\Delta G^0_{f,CeO2}$ =

  (Values will be presented)

ΔG^0_f of perovskites



Trends in free energy of formation for perovskites (AMO_3 = ABO_3), according to the atomic number of transition metal M.

Perovskites having equal oxidation states for A and M (+3, A=Y, La) are more stable than the ones having different (+2 and +4, A=Ca, Sr, Ba) and their decay in stability is less pronounced.

The positions of $La_{1-x}Sr_xMO_3$ support the idea that the effect is due to the oxidation states of the constituents.

From F. Calle-Vallejo et al., accepted for publication in *Angewandte Chemie,* 2010

Stability towards reaction with other materials

- $La_{0.8}Sr_{0.2}MnO_3$ (A/B = 1) reacts fast with $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ) at temperatures above 1000 and insulating phases of $La_2Zr_2O_7$ and $SrZrO_3$ are formed

- $(La_{0.8}Sr_{0.2})_{0.9}MnO_3$ (A/B = 0.9 nominally - a two phase system) does not react with $Zr_{0.84}Y_{0.16}O_{1.92}$ as long as it is not polarised

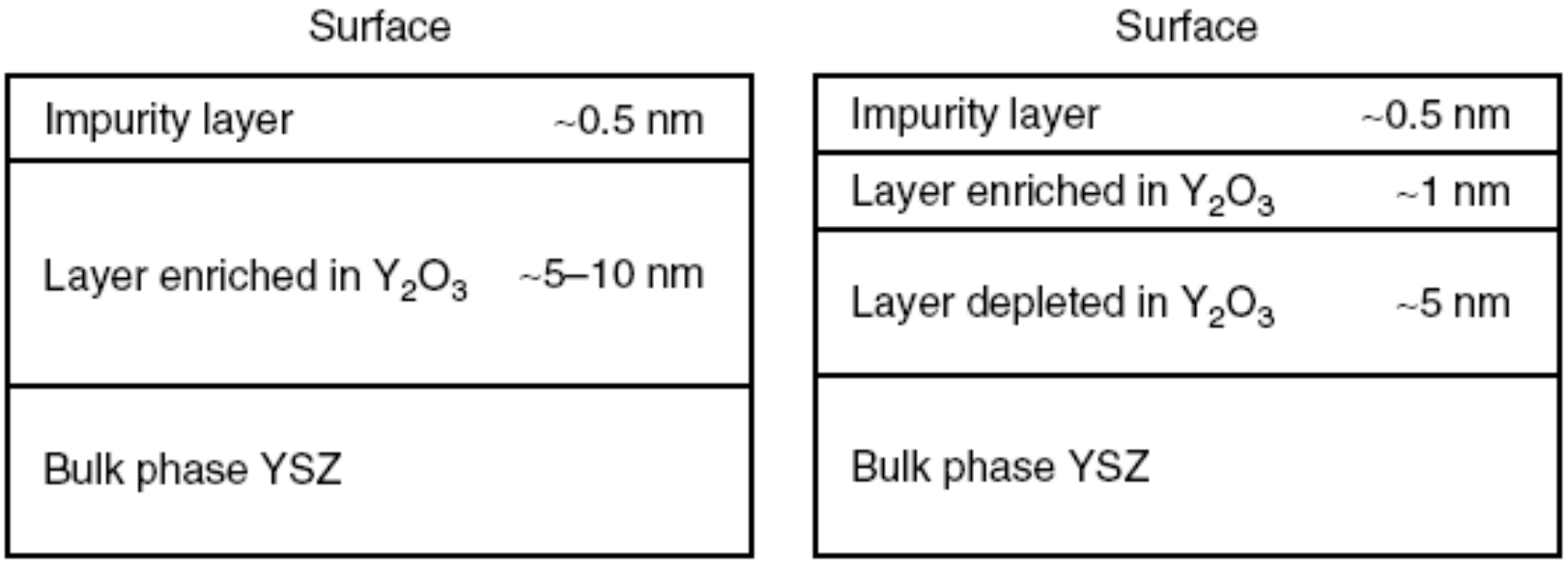
- $(La_{0.6}Sr_{0.4})_{0.9}Fe_{0.8}Co_{0.2}O_3$ reacts with YSZ irrespective of A/B ratio

- Such perovskites do not react with ceria the same way as with zirconia. The ionic radius of $Ce^{4+} > Zr^{4+}$.

Segregations to interfaces - impurities

The surface energy of clean fluorites and of many perovskites is high. This means that there is a pronounced tendency to segregate components and or impurities to the surface as this may decrease the free energy of the system. Everybody who examined such surfaces with the proper methods found the segregates even after short time (hours) at 500 °C.

Segregation to YSZ surfaces



Schematic representations of sandwich-type surface structures on YSZ with glassy surface layers of compositions of SiO2, Na2O, and CaO. (a) Near equilibrium after heat treatment at high temperatures (>1200 °C) for several hours. (b) Example of not-near equilibrium after sputtering the original surface away and a short annealing at 500 °C.

From: Fuel Cell Handbook, Vol 5, Chapt. 36.

Diffusion and defect chemistry - Kröger - Vink notation

- No diffusion and consequently no electrical conduction can take place in a defect free crystal
- Thus, the defect chemistry is very important and a special notation has been established, the Kröger - Vink notation:

- Using CeO_2 as an example: Ce_{Ce} is Ce^{4+} on the right Ce site, O_O is O^{2-} on right oxygen site, Ce'_{Ce} is a Ce^{3+} on Ce site, and $V^{\bullet\bullet}_O$ is an oxygen vacancy

- The defects are interpreted as chemical entities, e.g.:
- $O_O + 2Ce_{Ce} = V^{\bullet\bullet}_O + 2Ce'_{Ce} + 1/2\ O_2$ (gas)
- Pure CeO_2 is an insulator but after reduction (removal of some oxygen) CeO_{2-x} becomes a mixed ionic and electronic conductor (MIEC).
- **Defects are necessary!**

Properties necessary in SOFC

Fluorite possibilities:

- Good oxide ion conductivity
- High stability
- Simple - two components in starting point
- Modest electron conductivity
- *Good electrolytes*

Perovskite possibilities:

- Good oxide ion conductivity
- Good electron conductivity
- Some are highly stable
- Less simple – three components as starting point
- *Good for electrodes*

Both ion and electron conductivity needed in electrodes. Therefore, composites of fluorites and perovskites are often made in order to optimize electrodes.

This is possible due to low reactivity and fair TEC matching between some of the members of the two groups.

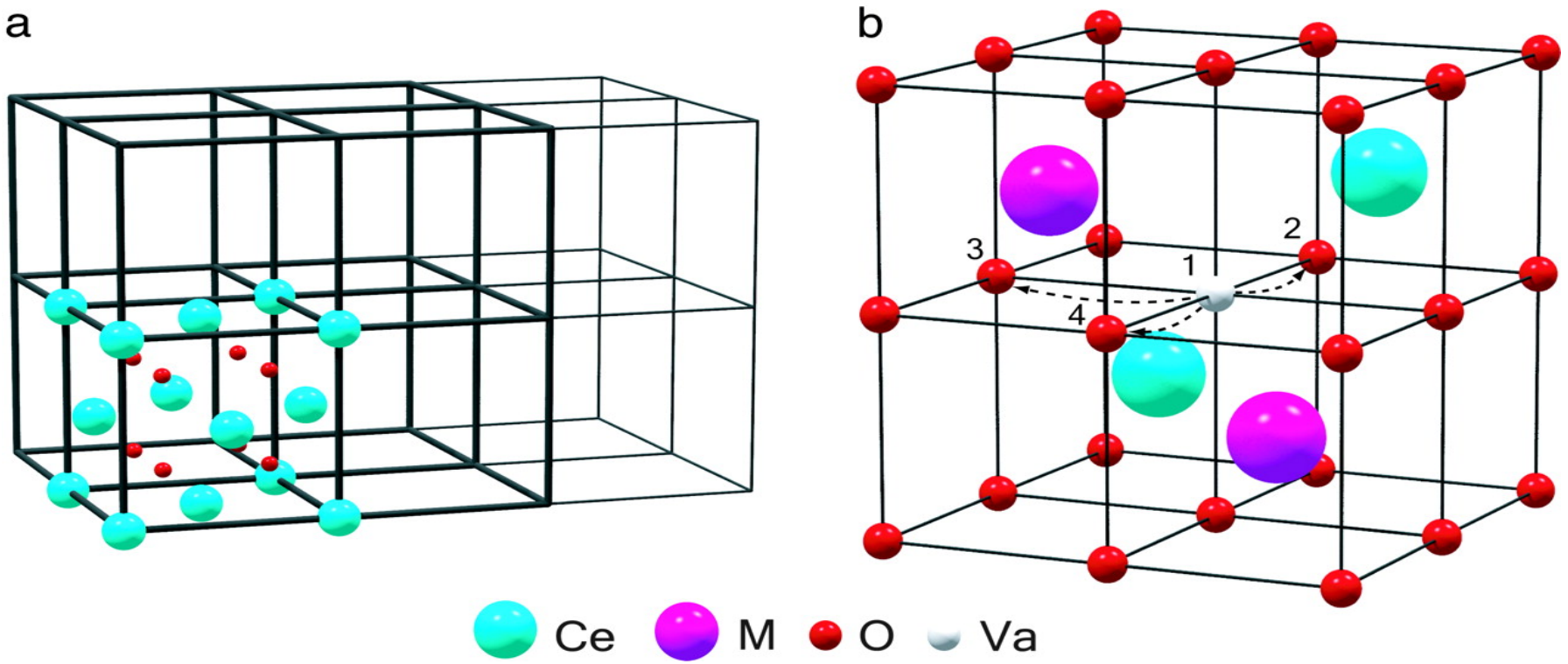
Optimization of properties

We published some years ago a paper with rules of thumbs for optimization of the oxide ion conductivity in these two materials groups:

M. Mogensen, D. Lybye, N. Bonanos, P.V. Hendriksen, F.W. Poulsen, "Factors controlling the oxide ion conductivity of fluorite and perovskite structured oxides", *Solid State Ionics*, 174 (2004) 279-286.

A brief explanation and summary of these rules are given after a look at the crystal structures

Fluorite structure: Cubic - else not Fluorite

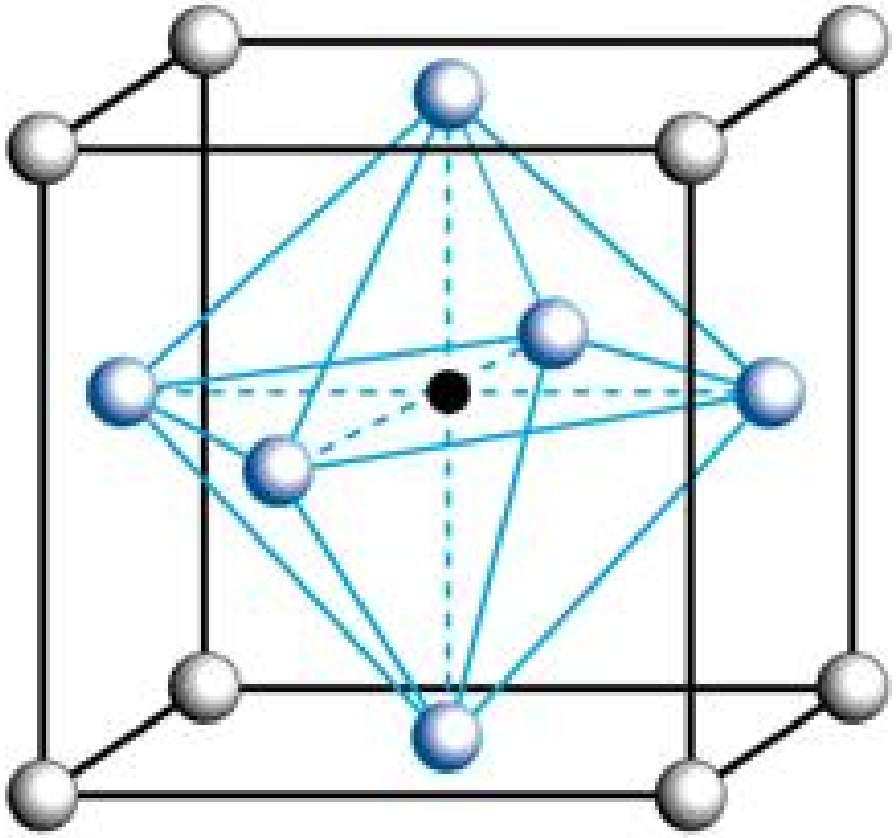


Wrong size of ions shown - if correct, too compact to be illustrative

r_{Ce4+} = 0.97 Å, r_{O2-} = 1.40 Å

Perovskite

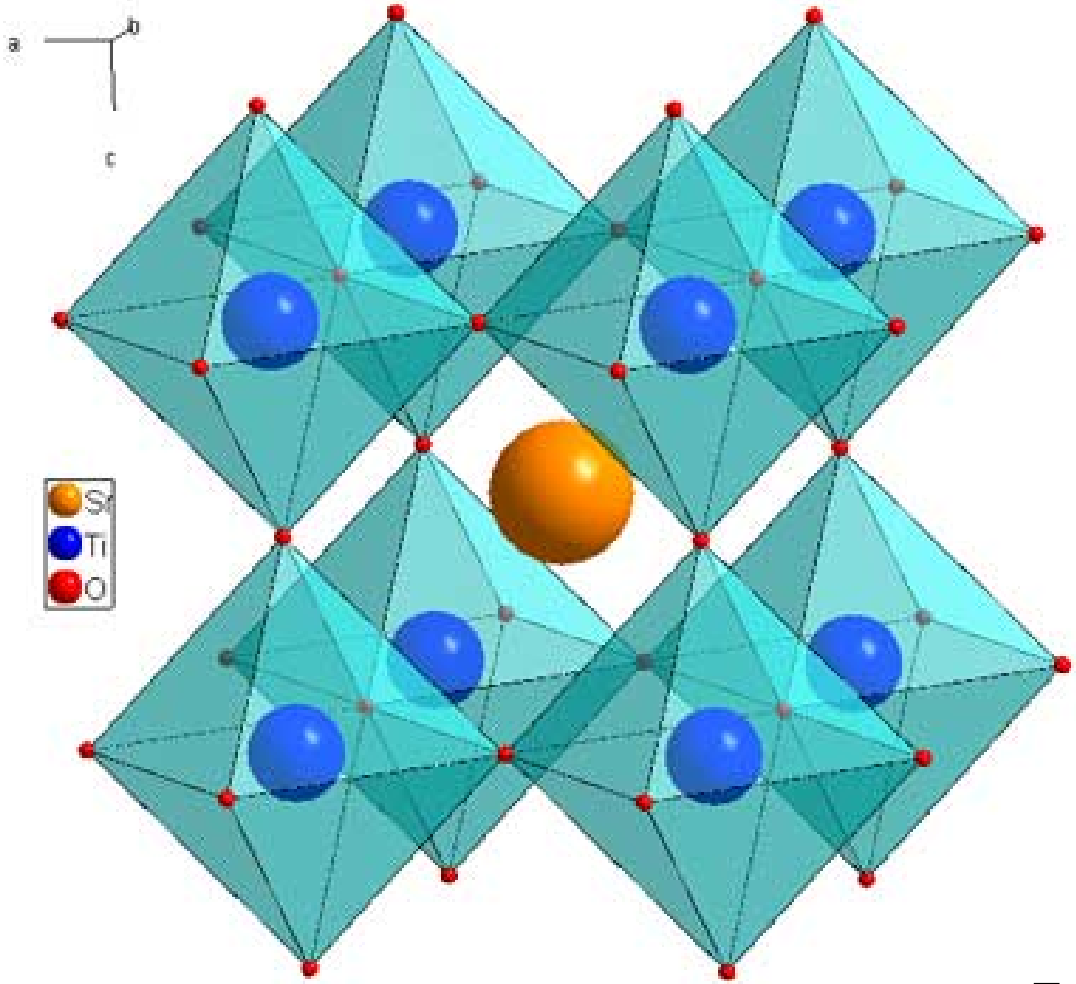
After V. P. Dravid



The O + A ions form together a cubic closest packed structure if the size of the A-ion is close to the size of the oxide ion.

Perovskite structure (Grey atoms: A, Black: B, Blue: O)

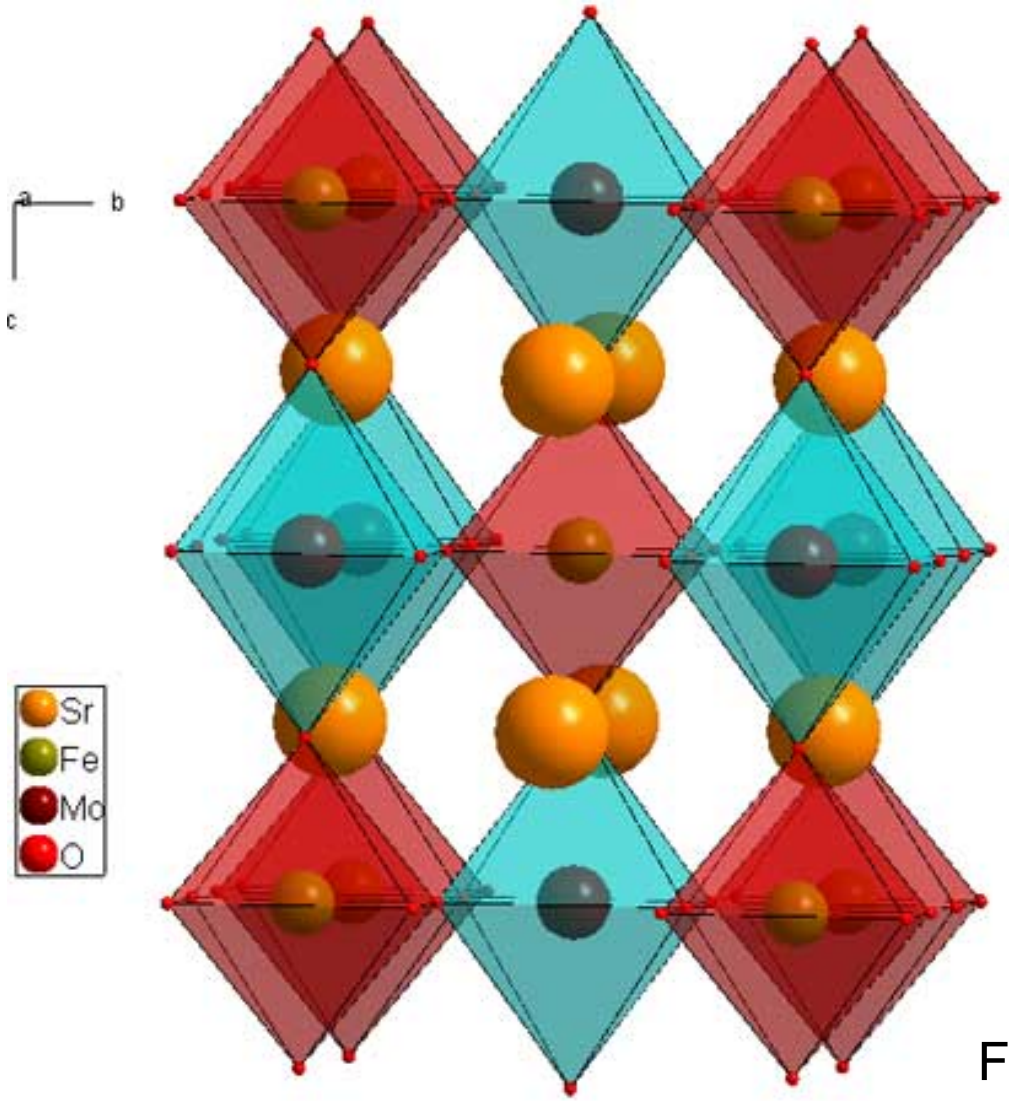
Perovskite
Often “distorted” cubic



$SrTiO_3$

From Cava Lab (J.R. Cava)

Double perovskites



Sr_2FeMoO_6

From Cava Lab (J.R. Cava)

Conductivity optimization

Generally accepted criteria for high oxide ion conductivity are:
1) High concentration of mobile charge carriers, i.e. of oxide vacancies
2) The energy of the oxide sites has to be equal or only slightly different, i.e. high symmetry
3) Weak bonding energy resulting in a relatively low melting point
4) Open paths between oxide ion sites

Note: The proposed parameters are all related to the ionic radii of the constituent cations, and therefore redundant

Stress free lattice

D.-J. Kim, *J. Am. Ceram. Soc.*, 72, 1415 (1989). : the solubility limit of a solute depends on the elastic energy, W, due to differences in ionic radii

$$W = 6Ga_0(\Delta a)^2$$

G is the shear modulus
a_0 is the lattice parameter
Δa, the change in a_0 by the solute of a given concentration.

Vegard's rule says: a linear relationship exists between lattice parameter and the concentration of the solute. The slope of the line is Vegard´s slope. If Vegard´s slope is zero then $\Delta a = 0$ and $W = 0$ for all concentrations.

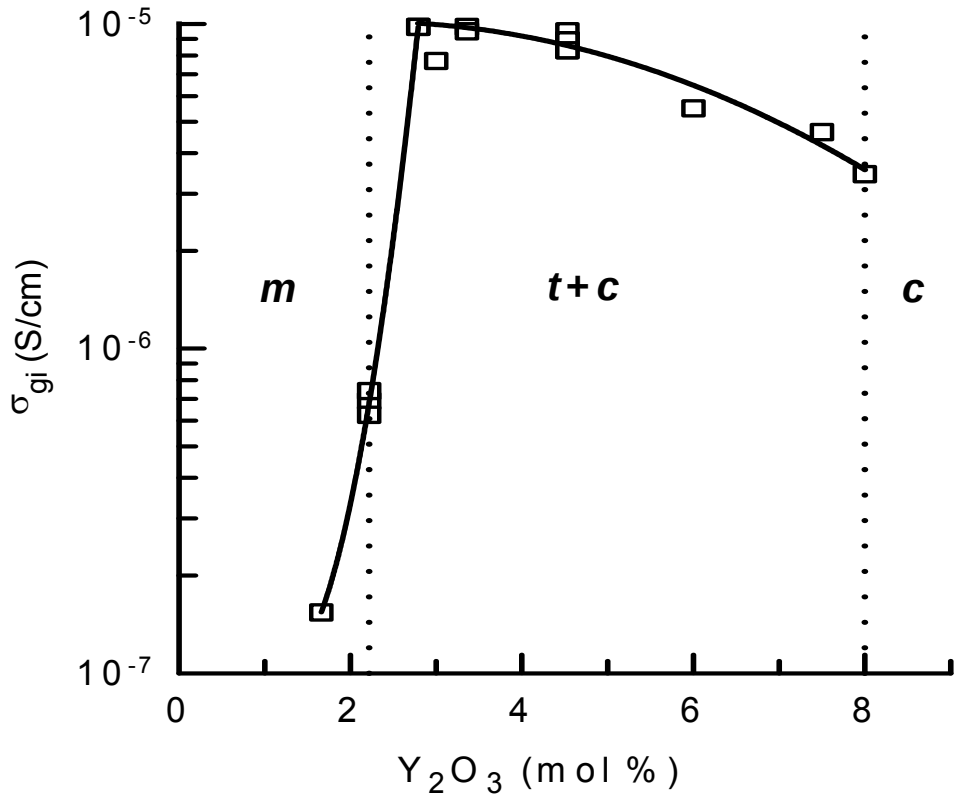
We call this for the stress free and the ion radius of a solute cation that gives a stress free lattice is the matching radius, r_m.

Matching radius

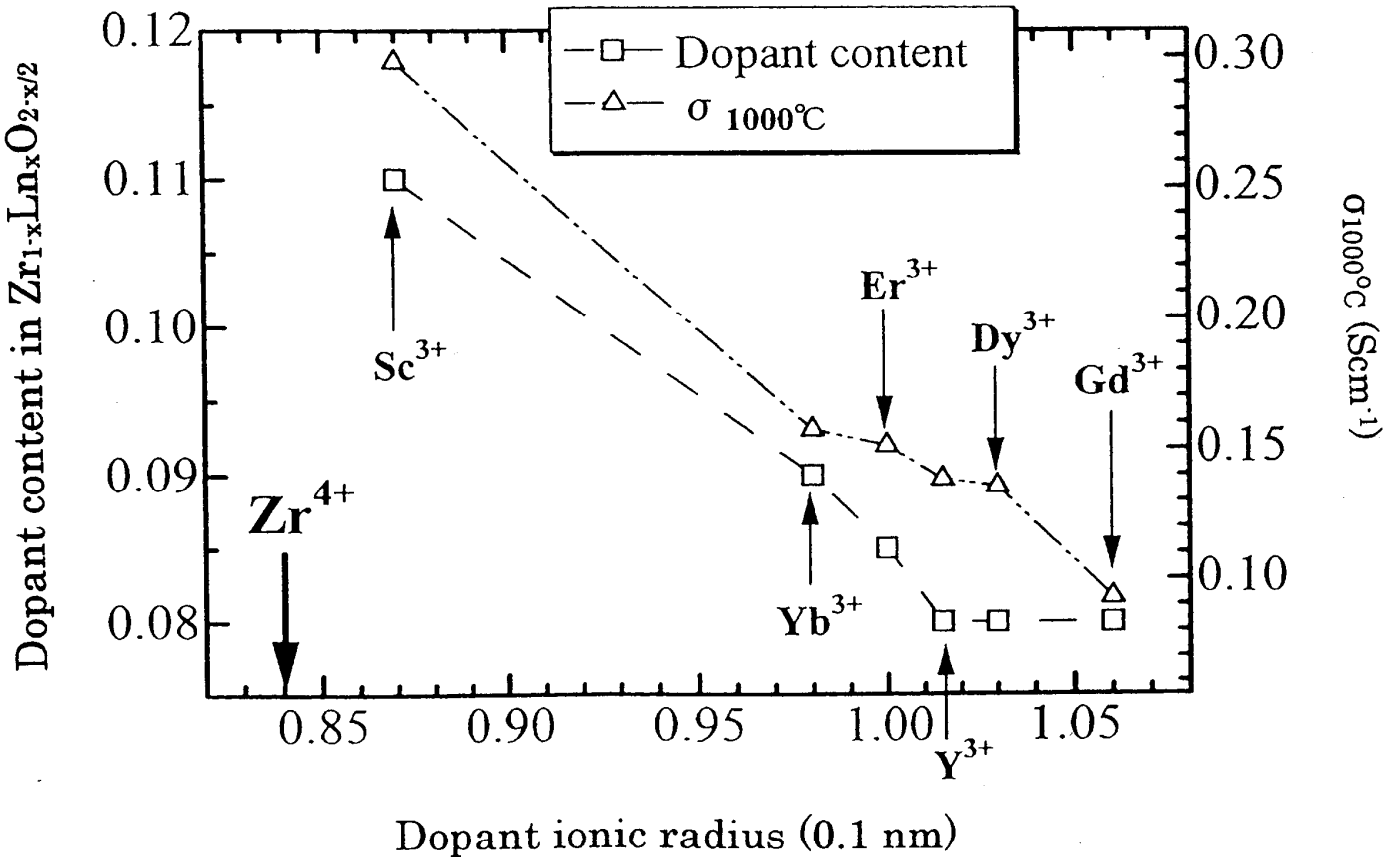
- The literature data shows for fluorite oxides that
- dopants with radii close to the matching radius have the high solubility values and thus allow the highest defect concentrations
- the mobility of the oxide ion is the larger, the closer the dopant radius is to the matching radius
- For zircona, r_m = 0.95 Å for trivalent ions (compared to r_{Zr4+} = 0.84 Å)
- For ceria, r_m = 1.04 Å for trivalent ions (compared to r_{Ce4+} = 0.97 Å)

Fluorites

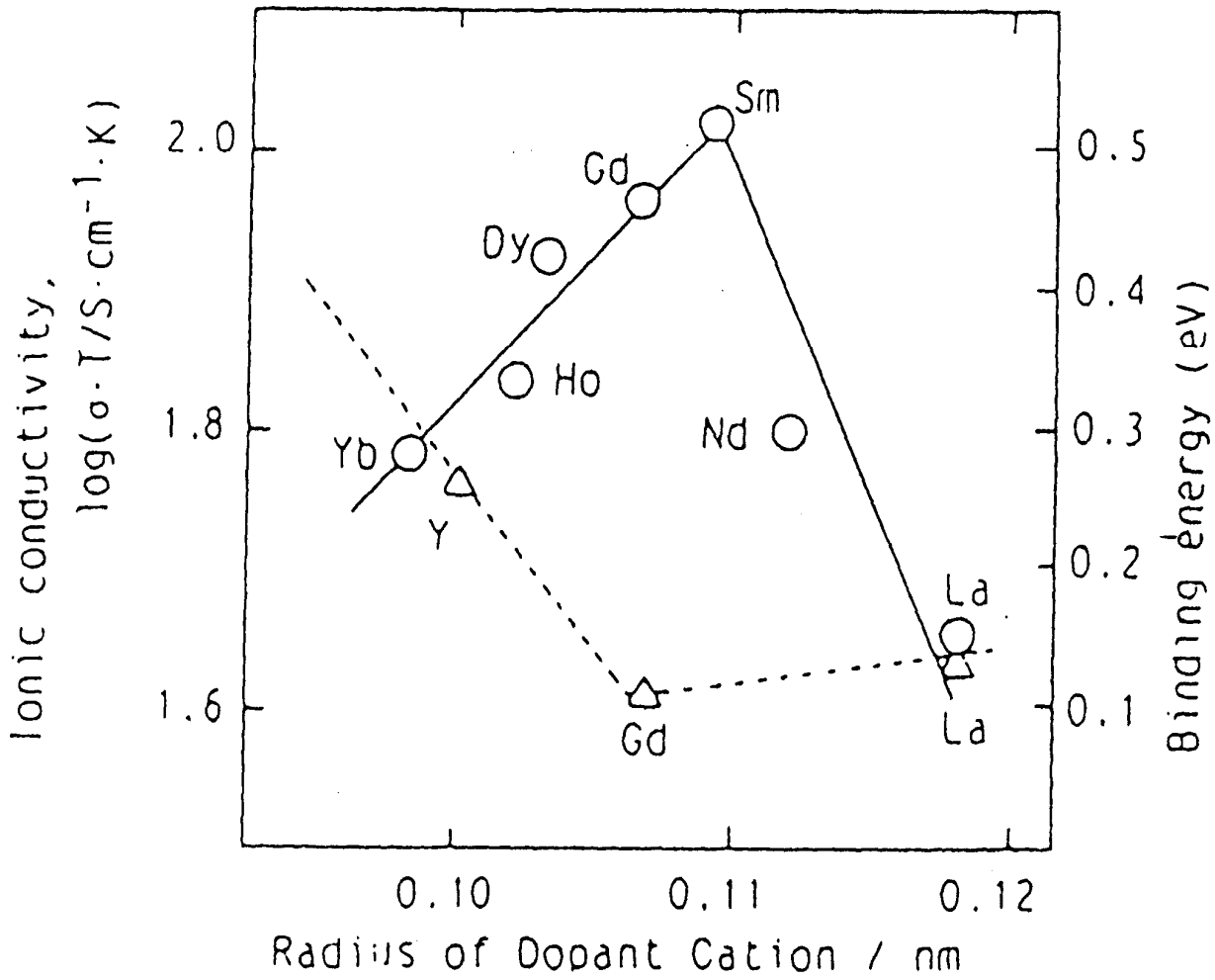
An "open" structure with a simple cubic oxygen lattice. Cations are inside every second oxygen cube.
The degree of symmetry of the crystal lattice is very important.



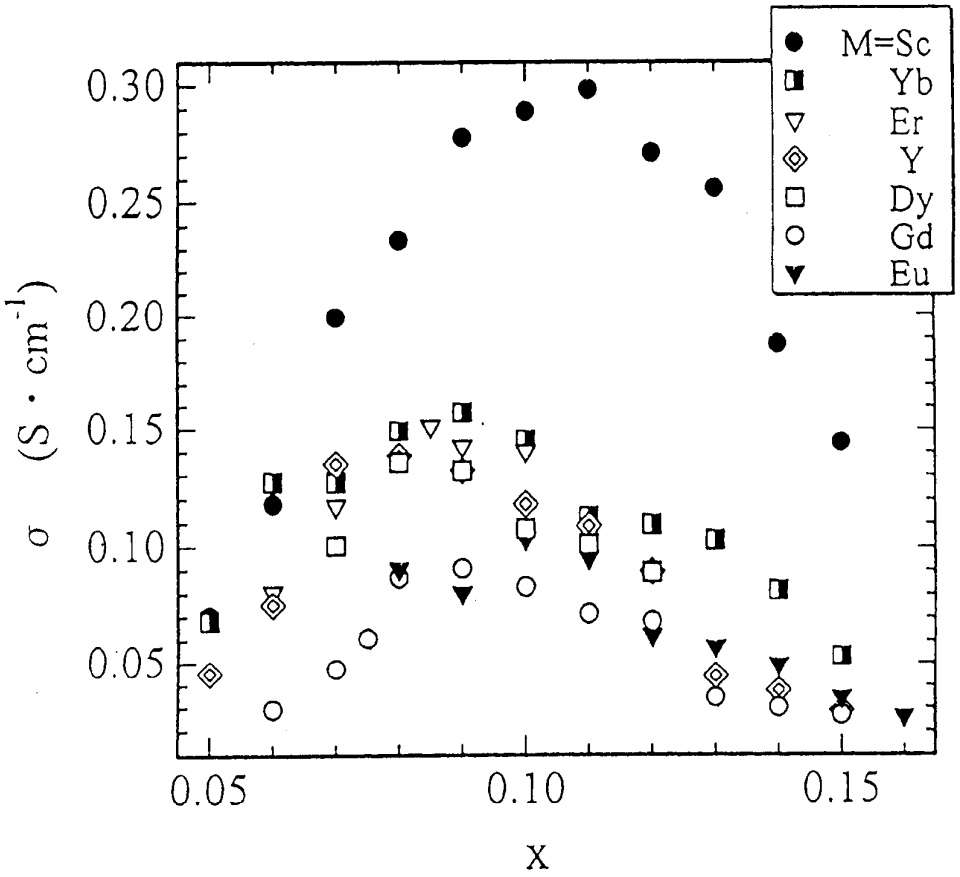
Conductivity of zirconia vs yttria content at 300 °C. The crystal structures are indicated by *m* for monoclinic, *t* for tetragonal and *c* for cubic



Dopant concentration exhibiting the highest conductivity dependence on dopant cation radius in ZrO_2–M_2O_3 systems.



Dependence of ionic conductivity for $(CeO_2)_{0.8}(Ln_2O_3)_{0.2}$ at 800°C on ionic radius of Ln^{3+}.



Composition dependence of the electrical conductivity at 1000°C for ZrO_2–M_2O_3 compositions.

From: T. Ishihara, N.M. Sammes, O. Yamamoto, in: *High Temperature Solid OxideFuel Cells: Fundamentals, Design and Applications*, S.C. Singhal, K. Kendall, Eds., p.83, Elsevier Ltd., (2003)

Conclusion on fluorites

- The stress free lattice results in the highest concentrations of oxide vacancies (charge carriers) and the highest mobility of the carriers, i.e. the highest conductivity.
- Thus, the best O^{2-} - conductors are obtained if the dopant ion radius is close to a value r_m (matching radius) that by substitution does not change the lattice parameter of the host oxide.
- Exception: the scandia - zirconia - system has the highest conductivity, and more than 10 times higher than expected, because Sc^{3+} is slightly smaller than r_m for zirconia. Sc has much lower atomic mass (45) than Y (89) and Yb (173).
- An optimum concentration exists for all dopants due to vacancy - dopant interaction.
- Other ion properties such as "preferred coordination number" are most probably of importance.

Perovskite

If the Goldschmidt tolerance factor

$$G_t = (r_A + r_O) / (\sqrt{2}(r_B + r_O))$$

is close to 1 the ideal cubic symmetry is obtained.

As for the fluorites also for the perovskites:

Symmetry and stress free lattice will give the maximum oxide ion conductivity, and matching radii may be defined.

Perovskite

- In case of the fluorites, each host metal oxide has it own matching radius.
- In the perovskite case, where the undistorted lattice is defined by the A-site and oxide ions together constituting a cubic closest packing, only one set of matching radii ($r_{m,A}$, $r_{m,B}$) exists.
- ($r_{m,A}$, $r_{m,B}$) = (1.4 Å, 0.6 Å)
- This explains why La3+ (r = 1.36Å in 12-fold coordination) and Sr2+ (r = 1.44 Å) usually are the best A-site ions for maximizing the conductivity.

Perovskite

In a defect free perovskite lattice the matching B-ion radius should be the “radius” of the octahedral hole, r_{oh} = 0.58 Å
In case of high oxide vacancy concentration:

The first row transition metal ions (Ti^{4+}, Cr^{3+}, …, Ni^{3+}) and Ga^{3+} typically have ionic radii between 0.55 and 0.65 Å.

$La_{1-x}Sr_xGa_{1-y-z}Mg_yCo_zO_3$ with suitable values of x, y and z is the best ion conductor of the stable perovskites

Perovskite

- On top of this the charge of the B-site ion is important as the oxide bonding to the small B-ion is much stronger than to the large A-ion.

- Thus, the 0,6 (MoO_3, WO_3) has the strongest bonding of the O, and the 3,3 (e.g. $LaCoO_3$) has the weakest boding of the O, i.e. has the highest ionic conductivity.

BSCF?

- $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ apparently breaks all the rules. The Ba^{2+} is far too big.

- However, it is not thermodynamically stable, and only to some extent kinetically stable. So it does not “count” wrt the rules.

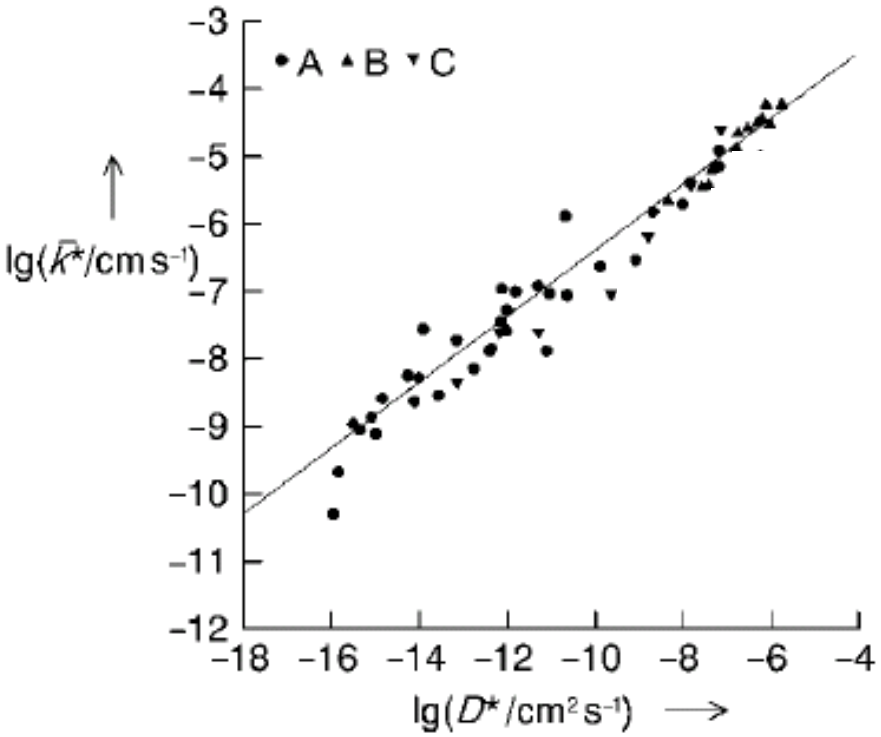
- Yet, it is still very interesting

Electron conductivity of perovskites

- If the rule is fulfilled, the symmetry is also maximized.
- The best electron conducting perovskites are also having close to perfect symmetry. Multi-valent metal atoms are necessary, e.g.

  $La_{1-x}Sr_xCoO_3$.
- Overlap between Co-d- and O-p orbitals is favored by cubic symmetry. Metallic type conductivity is then obtained.

Oxygen exchange on ABO_3



Correlation of the effective surface rate constant, k*, with the oxygen tracer bulk diffusion coefficient, D*. A: (La,Sr)(Mn,Co)O3-z, B: (Sm,Sr)(Co)O3-z, C: (La,Sr)(Co,Fe)O3-z for electron-rich transition metal perovskites.

D* is proportional to the vacancy concentration

From R. A. De Souza, J. Kilner, *Solid State Ionics*, **126** (1999) 153 – 161. The proposed relationship logk^* = -1 + 0.5 logD^* (given by the line) is from R. Merckle, J. Maier, H.J.M. Bouwmeester, *Angew. Chem. Int. Ed.*, **43**, (2004) 5069

All measured on single phase bodies/surfaces of the ionic materials using SIMS

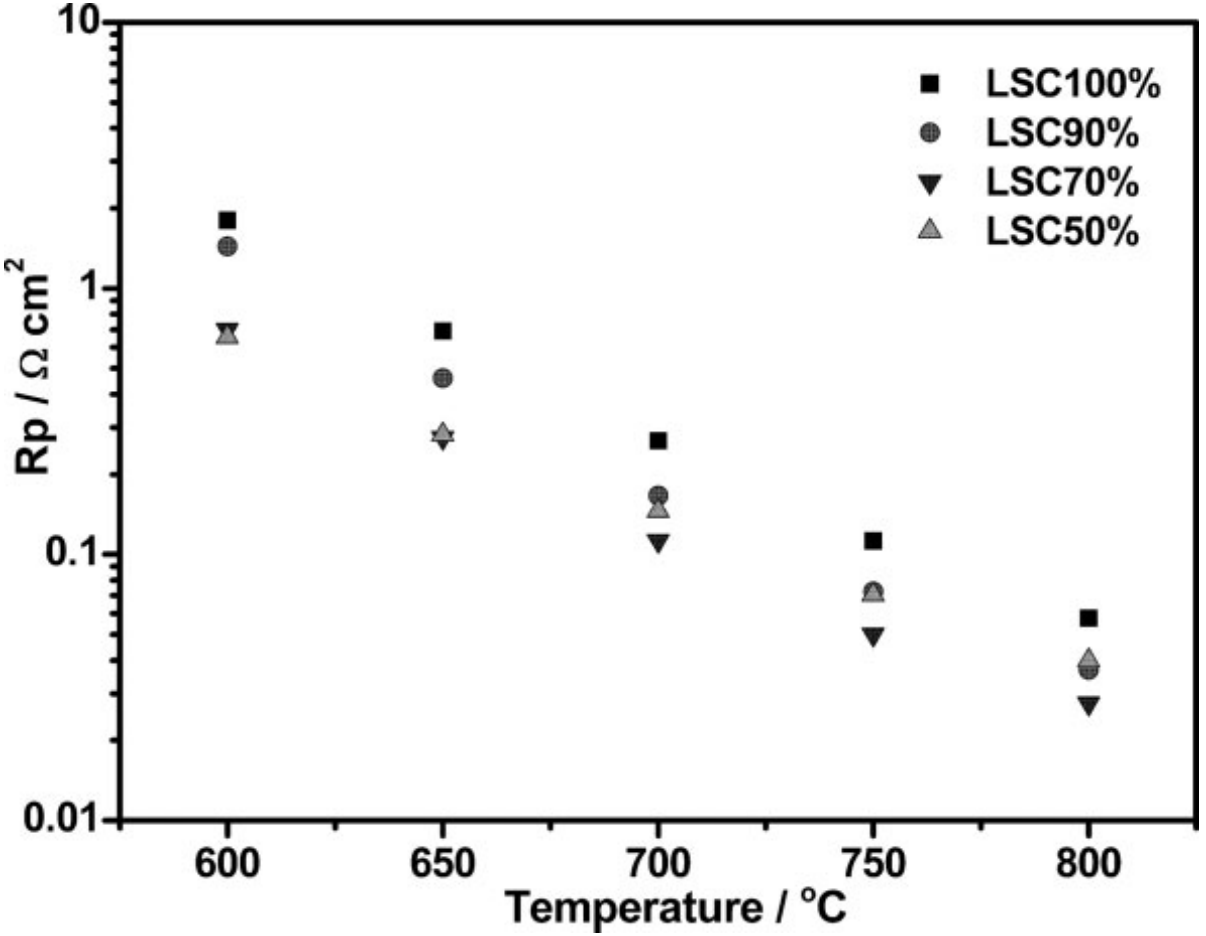
Conclusion on lattice effects

- **Both fluorites and perovskites properties are improved by doping as close to the matching radius as possible with respect to:**
- **ion conductivity**
- **electronic conductivity**
- **oxygen surface exchange rate**

Proton conduction in perovskites

- The “Proton conducting perovskites” is a book of its own, and not as well understood as the O^{2-} conduction.
- It is noteworthy that $BaZrO_3$ is nicely cubic with a Goldschmidt tolerance factor of 1.0, but the ionic radii of the host cations are far from matching radii for a perovskite.
- Doped $BaZrO_3$ is the class of metal oxides with some of the highest known specific proton conductivity values.

The advantage of composite



The dependence of polarization resistance on the GDC content of the LSC/GDC composite cathodes employed on GDC electrolyte. From Tao et al., FUEL CELLS, 9 (2009) 679–683.

Thermal Expansion Coefficients

Table 4 from H.U. Anderson, SSI 52 (1992) 33

Thermal expansion coefficient (TEC) of dopants between 25-1100 °C of LaCr03 as a function Dopant TEC (× 10 6/°C) [a)]

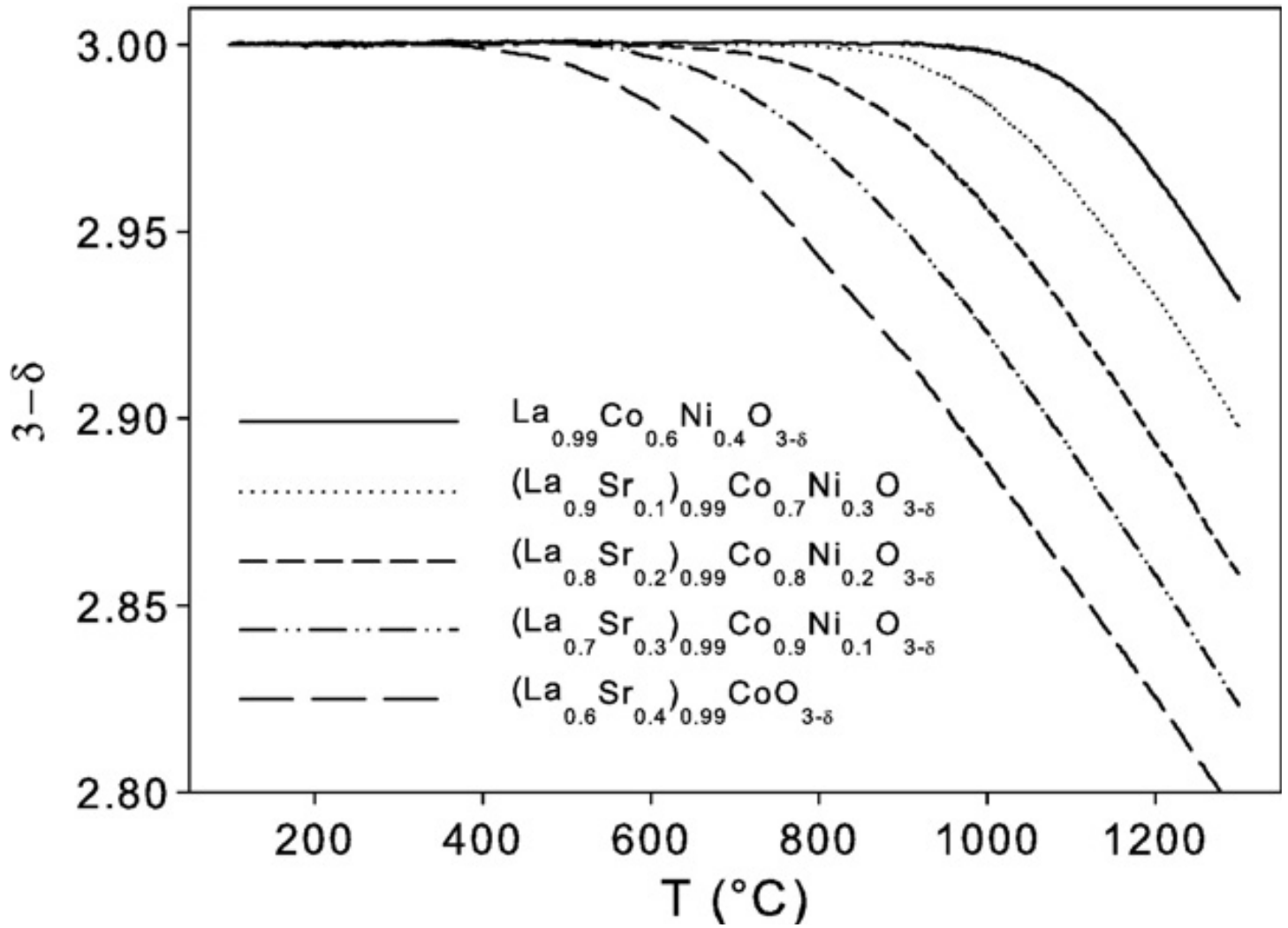
LaCrO3	9.5
10 % Mg-LaCrO3	9.5
2%Sr	10.2
10%Co	13.1
20% Co	13.6
30% Co	15.9
10 Co, 10 Ca	12.3
10 Co, 20 Ca	11.1
10 Co, 30 Ca	10.4
YSZ	10.3

[a)] 5% standard deviation.

Values from other sources (25 - 1000 °C):

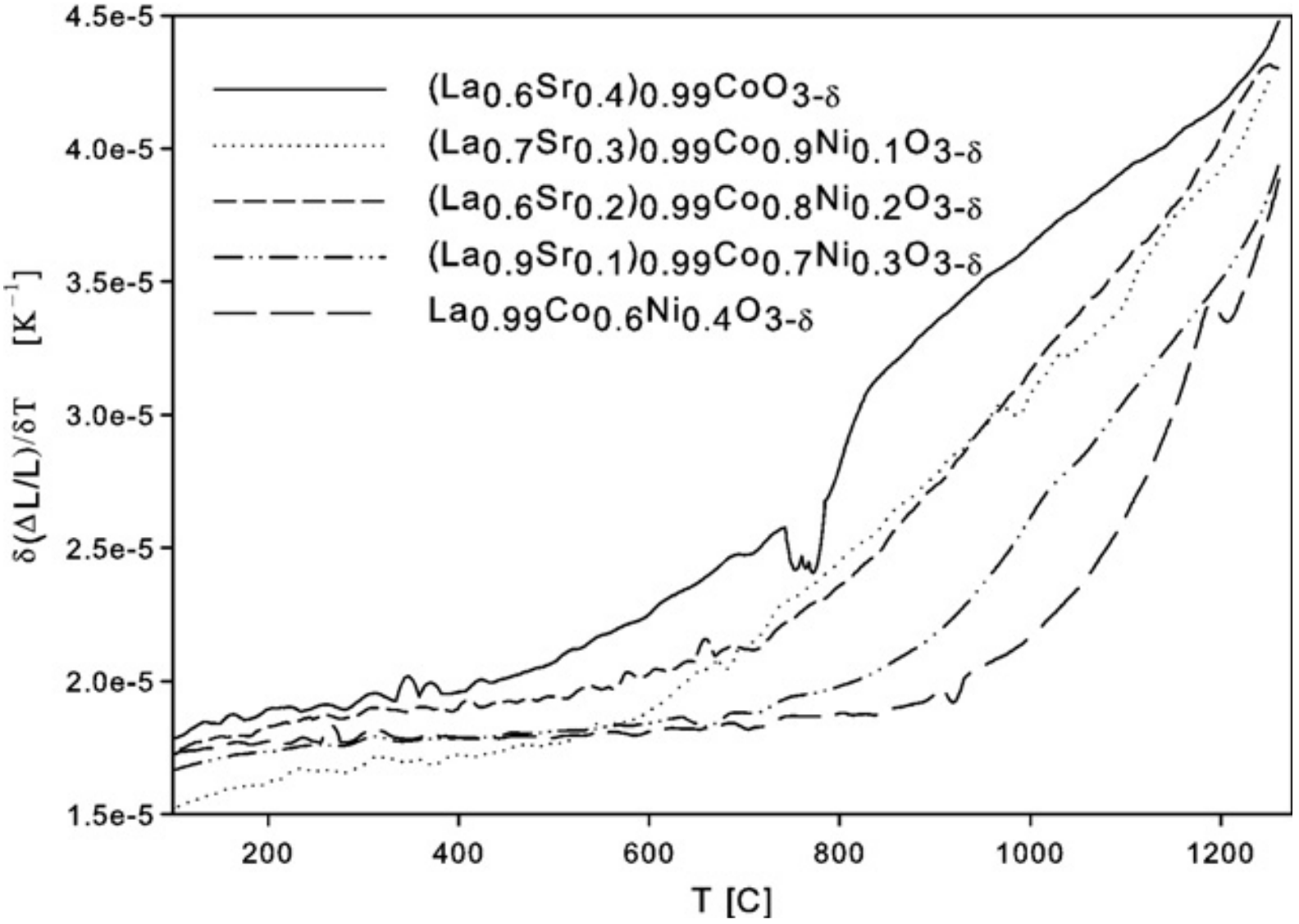
8YSZ	10. 8
GDC10	12.5

Instability of cobaltites



Hjalmarsson et al., Solid State Ionics 179 (2008) 636–646

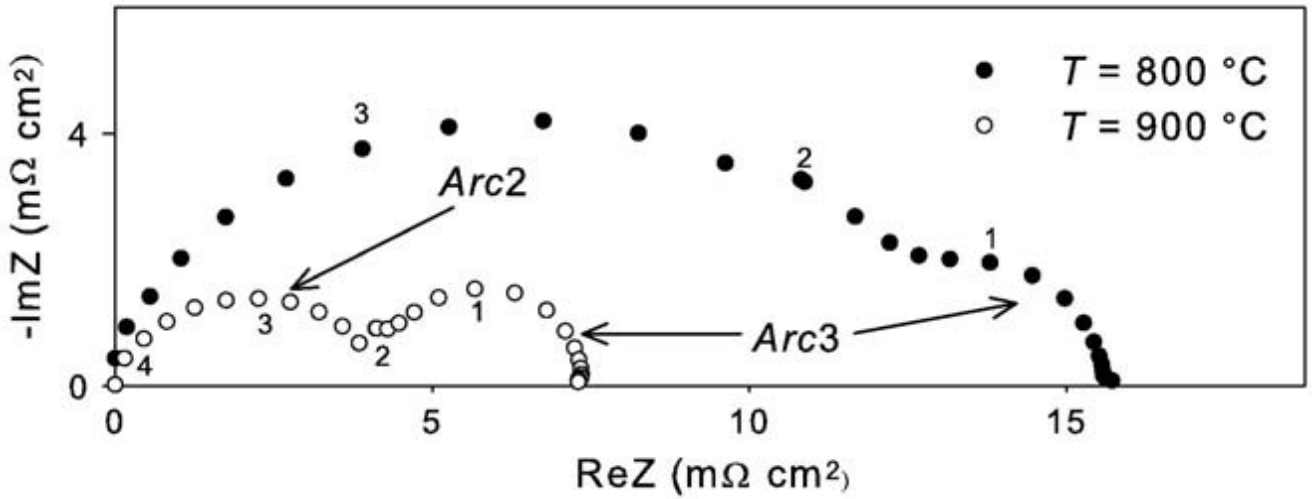
TEC and thermal reduction



TEC and SEC

- Thermal expansion coefficient, TEC, requires constant stoichiometry
- Expansions due to changes in stoichiometry are described by an stoichiometric expansion coefficient, SEC, measured as change in dimensions with change in stoichiometry
- The SEC is in many cases a limitation for the use of perovskites as electrode backbones

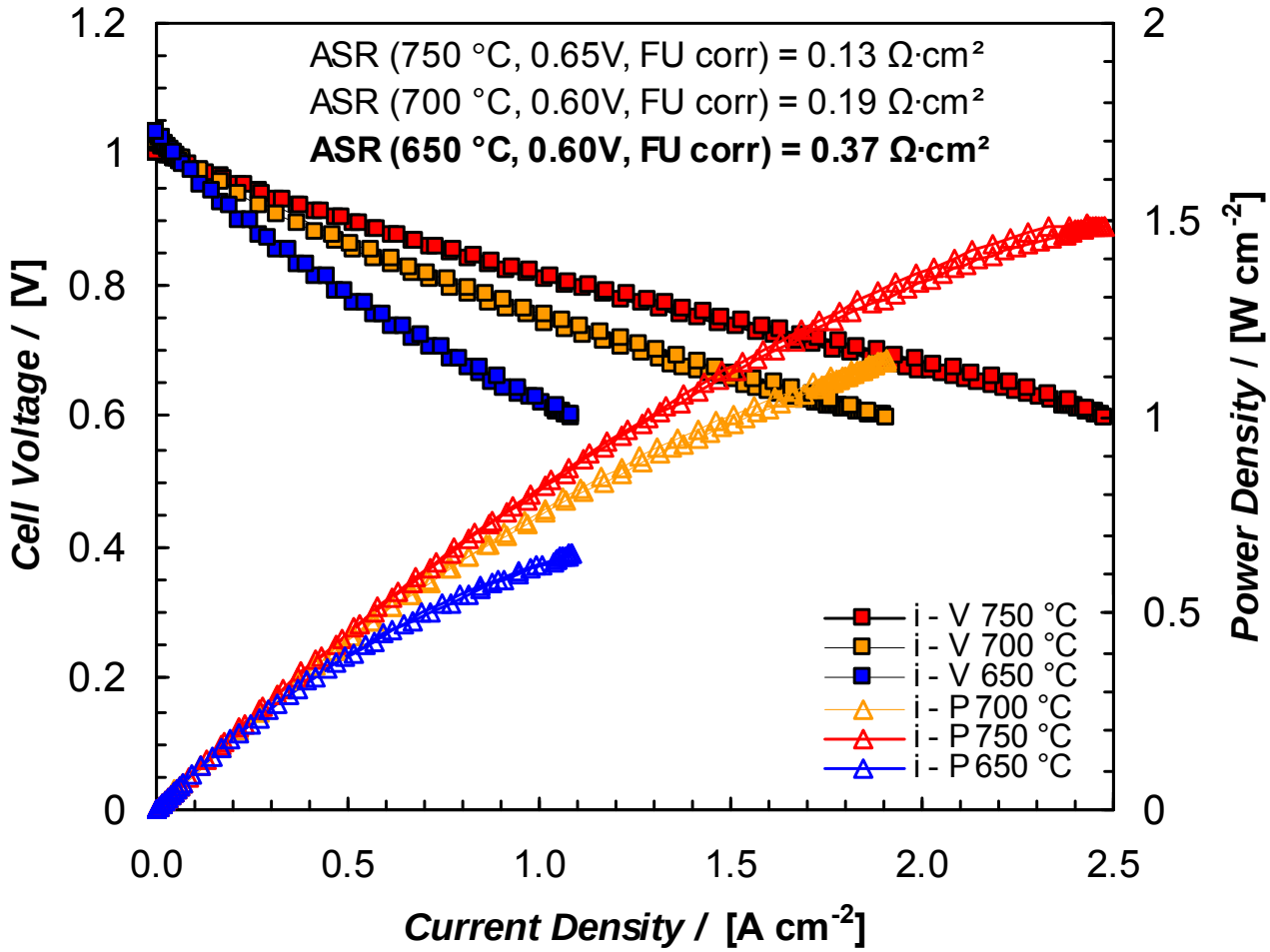
Example
Electrode performance



LSC cathode. Nyquist plots of the electrode response measured in ambient air. Serial resistance and inductance were subtracted from both spectra to ease comparisons. Numbers represent log-values of the frequencies. Per Hjalmarsson et al. Risø DTU.

Note! Units in mΩ cm²!

Cell performance



***i - V* and *i - P* curves for an SOFC anode supported Ni-YSZ / YSZ / CGO / LSC-CGO cell**

Recommended books

Hans Rickert, *Electrochemistry of Solids - An Introduction*, Springer-Verlag, 1982.

Subhash Singhal, Kevin Kendall *High Temperature SOFCs, Fundamentals, Design and Applications*, Elsevier 2003.

Joachim Maier, *Physical Chemistry of Ionic Materials*, Wiley 2004.

Thank you for your attention

Any questions?